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(54) Process for production of water-absorbent resin

Verfahren zur Herstellung eines wasserabsorbierenden Harzes

Procédé de préparation d'une résine absorbant de l'eau

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Description

The present invention relates to the production of a water-absorbent resin. More particularly, it relates to a process for the production of a water-absorbent resin having properties suitable for water-absorbent materials in the sanitary material field. The water-absorbent resin is cheap and has excellent productivity.

Recently, water-absorbent resins have been used in the field of sanitation such as in menstrual articles and diapers, in the fields of agriculture and horticulture, for example as water retention agents and soil conditioning agents and in industry, for example as cutoff materials and anti-dewing agents, and they have been used in various other applications. In particular, water-absorbent resins have been used with commercial success in the field of sanitation such as in menstrual articles and diapers.

These water-absorbent resins can be made from any suitable polymer which is lightly crosslinked, and examples thereof include hydrolyzates of starch-acrylonitrile graft copolymers (JP-B-49-43395), neutralized products of starch-acrylic acid graft copolymers (JP-A-51-125468), saponified products of vinyl acetate-acrylic acid ester copolymers (JP-A-52-14689) and partially neutralized polyacrylic acid products (JP-A-62-172006, JP-A-57-158209 and JP-A-57-21405).

Usually, the properties desired for water-absorbent resins are a high absorbency, an excellent water-absorption rate, a high gel strength after absorption of water, a shape suitable for application and conformability with a material with which it is to be used. In particular, the desired properties for water-absorbent resins used for sanitary materials are a high absorbency, a high water-absorption rate, a high gel strength after absorption of water, large particle size, less fine powder, a sharp distribution of particle size, integrity with a pulp, a small amount of reversion of absorbed substances to the exterior and excellent diffusion of absorbed substances into the interior of the absorbents. It can be said that a good water-absorbent material should satisfy these properties as well as be safe and cheap. Hitherto, water-absorbent resins have been mainly produced by solution polymerization or reversed phase suspension polymerization of water-soluble ethylenic unsaturated monomers, as disclosed, for example, in EP-A-0119078. In that process, a water-in-oil emulsion of the monomer is polymerized in the presence of a first highly reactive polymerization initiator until a small amount of polymer, sufficient to provide a shear stable emulsion, is present. Polymerization is then completed using a less reactive initiator. Among these processes, the production of water-absorbent resins by reversed phase suspension polymerization has the following disadvantages.

Firstly, a water-absorbent resin obtained by reversed phase suspension polymerization method of a water-soluble ethylenic unsaturated monomer is a powder of spherical particles having a sharp distribution of particle size in comparison with that obtained by subjecting the monomer to solution polymerization, followed by grinding. However, to date, a water-absorbent resin having large particle size could not be obtained. Secondly, since a surfactant and/or a polymeric protective colloid are used, they remain on the surface of the product and therefore initial wettability by water is inferior due to water repellency of the surfactant and/or polymeric protective colloid. As a means for mitigating this phenomenon and improving initial wettability by water, consideration has been given to removing the surfactant and/or polymeric protective colloid from a product by filtering a slurry obtained by reversed phase suspension polymerization and drying. However, purification of the filtrate is very expensive and such a process is far from an economical production process, although initial wettability by water is improved. Thirdly, the polymerization of a water-soluble ethylenic unsaturated monomer is an exothermic reaction and heat is generated within a short period of time. Therefore, in the reversed phase suspension polymerization, an increase in the amount of the monomer which may be present in a solvent is limited due to resultant difficulties in removal of heat. Accordingly, improvement of productivity by decreasing the amount of solvent and increasing the amount of monomer is limited. Fourthly, in the reversed phase suspension polymerization, the surfactant and/or polymeric protective colloid should be used, at least, in an amount sufficient for making a suspension in order to carry out a stable polymerization, and the amount cannot be reduced to less than this required minimum amount.

In order to solve the above problems, we have made intensive investigations. As a result, it has been found that, by carrying out the reversed phase suspension polymerization in multiple stages, a water-absorbent resin having large particle size, less fine powder, a sharp distribution and extremely excellent wettability by water in addition to excellent water absorption properties can be obtained, productivity can be highly improved and further the amount of a surfactant and/or polymeric protective colloid used can be reduced.

The present invention seeks mainly to provide an improved process for the production of a water-absorbent resin by reversed phase suspension polymerization of a water-soluble ethylenic unsaturated monomer.

This object as well as other objects and advantages of the present invention will be apparent to those skilled in the art from the following description.

According to the present invention, there is provided a process for the production of a water-absorbent resin, which process comprises, in a first polymerization stage, subjecting an aqueous solution of a water-soluble ethylenic unsaturated monomer to a reversed phase suspension polymerization reaction in a petroleum hydrocarbon solvent in the presence of a surfactant and/or polymeric protective colloid, which surfactant and/or polymeric protective colloid is present in an amount of from 0.1 to 5 wt%, based on the total weight of the aqueous monomer solution of the first stage using a radical polymerization initiator optionally in the presence of a crosslinking agent, cooling the resulting first stage polymerization reaction system to precipitate the surfactant and/or polymeric protective colloid, and then, for at least a

second polymerization stage, adding, at least once, an aqueous solution of a water-soluble ethylenic unsaturated monomer solution containing a radical polymerization initiator and optionally a crosslinking agent to the first stage polymerization reaction system to carry out a further reversed phase suspension polymerization reaction.

The invention will now be described in more detail.

In the process of the present invention, the reversed phase suspension polymerization reaction is carried out in multiple stages, ie in at least two stages, and may be carried out in three or more stages. Since, usually, the desired result can be obtained by a polymerization reaction of two stages, the two stage reaction is mainly explained below.

That is, according to the process of the present invention, for carrying out the two stage reaction, an aqueous solution of a water-soluble ethylenic unsaturated monomer is firstly polymerized in a petroleum hydrocarbon solvent in the presence of a surfactant and/or polymeric protective colloid by using a radical polymerization initiator optionally in the presence of a crosslinking agent. Then, after this first polymerization stage, the resulting slurry is cooled so that the surfactant and/or polymeric protective colloid are precipitated in the solvent to prevent suspension of an aqueous solution of the monomer for the second stage. Then, the monomer solution of the second stage is added and absorbed on to a water-containing gel produced by the first polymerization stage and the second polymerization stage is carried out.

When the monomer solution for the second polymerization stage is added to the reaction system under conditions such that the surfactant and/or polymeric protective colloid are dissolved in the solvent after the completion of the first polymerization stage, the monomer solution is suspended before it is absorbed on to the water-containing gel obtained by the first polymerization and, therefore, the particle size of the resulting product becomes small and the distribution thereof becomes broad. On the contrary, when the monomer solution of the second stage is added to the reaction system under conditions such that the surfactant and/or polymeric protective colloid are precipitated in the solvent, the water-containing gel obtained by the first polymerization is hardly effected by surface activities of the surfactant and/or polymeric protective colloid and, therefore, a water-absorbent resin having a large particle size, less fine powder and a sharp distribution of particle size can be obtained.

Furthermore, wettability by water of the resulting water-absorbent resin is remarkably improved. Perhaps, this results from envelopment of the surfactant and/or polymeric protective colloid with the monomer solution of the second polymerization stage upon absorption of the solution on to the water-containing gel obtained by the first polymerization stage.

The water-soluble ethylenic unsaturated monomer used may be any of conventional monomers. Examples thereof include (meth)acrylic acid, 2-(meth)acrylamide-2 methylpropanesulfonic acid and/or alkali salts thereof, nonionic monomers such as (meth)acrylamide, N,N-dimethyl acrylamide, 2-hydroxyethyl(meth)acrylate, and N-methylol(meth)acrylamide, amino group-containing unsaturated monomers such as diethylaminoethyl(meth)acrylate, diethylaminopropyl(meth)acrylate, and dimethylaminopropyl(meth)acrylate, and quarternized products thereof. They are used alone or in combination with one another. (The term "(meth)acryl" used herein means both "acryl" and "methacryl".) Among them, acrylic acid, methacrylic acid or alkali salts thereof, acrylamide, methacrylamide and N,N-dimethylacrylamide are preferred. Furthermore, the monomer component used in the second and subsequent stages may be the same as or different from that used in the first stage. In general, the monomer concentration in the aqueous solution of a water-soluble ethylenic unsaturated monomer in each stage may be not less than 25% by weight, and is preferably from 25% by weight up to its saturated solution concentration.

Any surfactant and polymeric protective colloid can be used in so far as the reversed phase suspension polymerization can proceed to complete the first polymerization stage, and they can be used in combination with one another. Examples of the surfactant which can be used are nonionic surfactants such as one or more of sorbitan fatty acid ester, polyglycerin fatty acid ester, sucrose fatty acid ester and sorbitol fatty acid ester, or polyoxyethylene alkylphenyl ether. Examples of the polymeric protective colloid which can be used are one or more of ethyl cellulose, ethyl hydroxyethyl cellulose, oxidized polyethylene, polyethylene modified with maleic anhydride, polybutadiene modified by maleic anhydride and EPDM (ethylene-propylene-diene-terpolymer) modified with maleic anhydride. Furthermore, anionic surfactants such as fatty acid salts, alkyl benzenesulfonate salts, alkyl methyltaurate salts, polyoxyethylene alkylphenyl ether sulfate and polyoxyethylene alkyl ether sulfonate can also be used in combination with the nonionic surfactants and/or polymeric protective colloid.

The amount of these surfactants and/or polymeric protective colloids used is 0.1 to 5% by weight, preferably 0.2 to 3% by weight, based on the total weight of the aqueous monomer solution for the first stage.

The petroleum hydrocarbon solvent used is, for example, an aliphatic hydrocarbon, cycloaliphatic hydrocarbon or aromatic hydrocarbon. As aliphatic hydrocarbon, n-pentane, n-hexane, n-heptane and ligroin are preferred. As the cycloaliphatic hydrocarbon , cyclopentane, methylcyclopentane, cyclohexane and methylcyclohexane are preferred. As the aromatic hydrocarbon , benzene, toluene and xylene are preferred. In particular, one or more of n-hexane, n-heptane, cyclohexane, toluene and xylene can be advantageously used because they are easily available and cheap in addition to their stable industrial quality.

The crosslinking agent optionally used in the first stage and the second and subsequent stages is that having at least two polymerizable unsaturated, groups and/or reactive functional groups. Examples of the crosslinking agent having at least two polymerizable unsaturated groups include di- or tri(meth)acrylate esters of polyols such as ethylene glycol, propylene glycol, trimethylolpropane, glycerin polyoxyethylene glycol, polyoxypropylene glycol and polyglycerin, unsatu-

rated polyesters obtained by reacting the above polyols with unsaturated acids such as maleic acid and fumaric acid, bisacrylamides such as N,N'-methylene bisacrylamide, di- or tri(meth)acrylate esters obtained by reacting polyepoxide with (meth)acrylic acid, di(meth)acrylate carbamyl esters obtained by reacting polyisocyanates such as tolylene diisocyanate and hexamethylene diisocyanate with, for example, hydroxyethyl (meth)acrylate, allylated starch, allylated cellulose, diallyl phthalate, N,N',N''-triallyl isocyanurate and divinylbenzene.

Among these, ethylene glycol diacrylate, ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, propylene glycol diacrylate, propylene glycol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, diallyl phthalate, N,N',N''-triallyl isocyanate and N,N'-methylene bisacrylamide are usually used.

The crosslinking agent having at least two reactive functional groups is, for example, a diglycidyl ether compound , haloepoxy compound or isocyanate compound. Among these, the diglycidyl ether compound is particularly suitable. Examples of the diglycidyl ether include (poly)ethylene glycol diglycidyl ether, (poly)propylene glycol glycidyl ether and (poly)glycerin glycidyl ether. Among these, ethylene glycol diglycidyl ether provides most preferred results. (The term "(poly)ethylene glycol" used herein means both "ethylene glycol" and "polyethylene glycol"). Furthermore, examples of the haloepoxy compound include epichlorohydrin, epibromohydrin and α-methylepichlorohydrin and examples of the isocyanate compound include 2,4-tolylene diisocyanate and hexamethylene diisocyanate. Any of these compounds can be used in the present invention. In general, the crosslinking agent is used in an amount of 0.001 to 5% by weight based on the weight of the monomer.

As the radical polymerization initiator used, conventional water-soluble radical polymerization initiators such as potassium persulfate, ammonium persulfate and sodium persulfate are suitable and these can be used in combination with, for example, a sulfite as a redox initiator. However, if an oil-soluble radical polymerization initiator is used, then since the resulting polymer generally becomes water-soluble, it should be used in the presence of a crosslinking agent. In this case, oil-soluble initiators such as benzoyl peroxide and azobisisobutyronitrile. It is preferred to use the radical polymerization initiator in an amount ranging from 0.005 to 1.0 mol% based on the monomer. When the amount is less than 0.005 mol%, it takes a very long time to carry out the polymerization reaction and, when the amount exceeds 1.0 mol%, a rapid polymerization reaction is caused, which is dangerous.

The polymerization temperature varies depending upon the polymerization initiator to be used. The polymerization temperature is usually 20 to 110°C, preferably, 40 to 80°C. When the polymerization is carried out at a temperature of higher than 110°C, it is difficult to remove the polymerization heat and, therefore, the polymerization cannot be smoothly carried out. When the polymerization is carried out at a temperature of lower than 20°C, the polymerization rate is lowered and a long polymerization time is required. This is not preferred from the economical viewpoint.

Precipitation of the surfactant and/or polymeric protective colloid after the polymerization of the first stage, which is one of the characteristics of the present invention, is carried out by cooling the reaction system. The cooling temperature varies depending upon the surfactant and polymeric protective colloid used as well as the type of solvent. For example, in the case of hexaglyceryl monobehenylate and n-heptane, the temperature is 38 to 40°C. In the case of hexaglyceryl monobehenylate and cyclohexane, the temperature is 27 to 30°C and, in the case of sorbitan monostearate and n-heptane, the temperature is 29 to 31°C.

The amount of the aqueous solution of the water-soluble ethylenic monomer containing the radical polymerization initiator and optionally the crosslinking agent used in the second and subsequent stages, which is absorbed on to the water-containing gel obtained by the first stage polymerization, is 50 to 300% by weight based on the total weight of the aqueous water-soluble ethylenic unsaturated monomer solution for the first stage.

When the amount of the aqueous solution of water-soluble ethylenic unsaturated monomer for the second and subsequent stages is less than 50% by weight, the desired various advantages of the present invention are hardly to be expected. On the other hand, when the amount is more than 300% by weight, the monomer solution is not completely absorbed during absorption of the second and subsequent stages and this is undesirable because it forms a mass or extremely large coarse particles.

The following Examples further illustrate the present invention in more detail.

In each Example, physical properties of the water-absorbent resin were determined according to the following methods.

(1) Absorbency

A water-absorbent resin (1 g) was dispersed in a 0.9% (w/w) aqueous solution of sodium chloride (200 ml), thoroughly swollen and then filtered through a 200 mesh metal wire net. The resulting swollen resin was weighed and the weight was taken as the absorbency.

(2) Water-absorption rate (wettability)

A water-absorbent resin (5 g) was spread over an area having a diameter of 3.5 cm in a Petri dish. Then, a 0.9% (w/w) aqueous solution of sodium chloride (2 cc) was added dropwise to this by means of a pipette and the period of time required for complete absorption of water was measured and the time was taken as the water wettability.

(3) Integrity with a pulp (evaluation of integrity with a carrier pulp for using the resin as an adsorbent)

A filter paper having a diameter of 11 cm was placed on a Petri dish and water (2 cc) was absorbed by the filter paper. A water-absorbent resin (2 g) was uniformly scattered on the filter paper. Then, the Petri dish was dried at 60°C for one hour and the amount of the water-absorbent resin adhered to the filter paper was measured and the amount was taken as the integrity.

(4) Measurement of reversion and diffusion

A water-absorbent resin (5 g) was uniformly scattered on a pulp sheet having a weight of 100 g/m^2 which was cut out to a size of 40 cm x 14 cm. The same pulp sheet as described above was laminated thereon and pressed by uniformly applying a pressure at 2 kg/cm^2 on the entire pulp surface to obtain an absorbent.

1.6% (w/w) Aqueous solution of sodium chloride (150 ml) was poured on the centre part of the absorbent thus prepared over 1 minute and the absorbent was allowed to stand for 10 minutes. Then, 20 sheets of filter paper (No. 2, manufactured by Toyo Roshi Co., Ltd.) cut out to a size of 10 cm x 10 cm were placed on the centre part and pressed by placing a weight of 3.5 kg (bottom surface area: 10 cm x 10 cm) thereon. The amount of liquid reverted was determined by measuring the amount of liquid absorbed in the filter paper.

Diffusion length was determined, by measuring spreading of the aqueous solution of sodium chloride.

Example 1

N-heptane (550 ml) was placed in a 1 liter four necked cylindrical round bottom flask equipped with a stirrer, a reflux condenser, a dropping funnel and a nitrogen gas inlet. To the flask was added hexaglyceryl monobehenylate having an HLB (hydrophile-lipophile balance) of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g). The surfactant was dissolved by heating at 50°C and the mixture was cooled to 30°C. separately, a 80% (w/w) aqueous solution of acrylic acid (92 g) was placed in a 500 ml conical flask and 20.1% (w/w) aqueous solution of sodium hydroxide (152.6 g) was added dropwise with external ice-cooling to neutralize 75 mol% of the acrylic acid. To the mixture was added potassium persulfate (0.11 g). The resulting partially neutralized acrylic acid solution was added to the above four necked round bottom flask and the reaction system was thoroughly purged with nitrogen gas. The reaction system was heated to carry out the polymerization reaction of the first stage, while maintaining the bath temperature at 70°C. The resulting polymerization slurry solution was cooled to 20°C, and the same amount of the partially neutralized acrylic acid solution prepared according to the same manner as described above was added dropwise to the reaction system and allowed to absorb for 30 minutes. At the same time, the system was thoroughly purged with nitrogen gas. The system was heated and subjected to polymerization of the second stage, while maintaining the bath temperature at 70°C. Water and n-heptane were distilled off and the residue was dried to obtain a water-absorbent resin (192.0 g) containing no fine powder and having a sharp distribution of particle size.

Example 2

According to the same manner as described in Example 1, the polymerization was carried out except that ethylene glycol diglycidyl ether (each 18.4 mg) was added as a crosslinking agent to the partially neutralized aqueous acrylic acid solution used in polymerization of the first and second stages to obtain a water-absorbent resin (192.5 g) containing no fine powder and having a sharp distribution of particle size.

Example 3

According to the same manner as described in Example 1, the polymerization was carried out except that a temperature in the system was adjusted to 25°C upon absorption of the partially neutralized aqueous acrylic acid solution used in polymerization of the second stage to the polymerization solution of the first stage to obtain a water-absorbent resin (192.8 g) containing no fine powder and having a sharp distribution of particle size.

Example 4

According to the same manner as described in Example 2, the polymerization was carried out except that 37% (w/w) aqueous solution of acrylamide (196.2 g) was used in place of the partially neutralized aqueous acrylic acid solution used in the polymerization of the second stage to obtain a water-absorbent resin (173.1 g) containing no fine powder and having a sharp distribution of particle size.

Example 5

According to the same manner as described in Example 2, the polymerization was carried out except that an aqueous monomer solution prepared by mixing a partially neutralized aqueous acrylic acid solution, which was obtained by mixing 80% (w/w) aqueous solution of acrylic acid (46 g) and 14.6% (w/w) aqueous solution of sodium hydroxide (104.8 g) to neutralize 75 mol% of the acrylic acid, and 30% (w/w) aqueous solution of acrylamide (120.9 g) was used for the polymerization of the first and second stages, respectively, in place of the partially neutralized aqueous acrylic acid solution used for the polymerization of the first and second stages to obtain a water-absorbent resin (172.5 g) containing no fine powder and having a sharp distribution of particle size.

Example 6

According to the same manner as described in Example 1, the polymerization was carried out except that sorbitan monostearate having HLB of 4.7 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion SP-60R) (2.76 g) was used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fate Co., Ltd. under the trade name of Nonion GV-106) (1.38 g) and the temperature in the system was adjusted to 15°C upon the absorption of the partially neutralized acrylic acid solution used in the polymerization of the second stage to the polymerization solution of the first stage to obtain a water-absorbent resin (194.0 g) containing no fine powder and having a sharp distribution of particle size.

Example 7

According to the same manner as described in Example 1, the polymerization was carried out except that sorbitan monolaurate having HLB of 8.6 (manufactured and sold by Nippon Oil and Fats Co., Ltd., Japan under the trade name of Nonion LP-20R) (0.97 g) was used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g), a partially neutralized aqueous acrylic acid solution used for the polymerization of the second stage was prepared by mixing 80% (w/w) aqueous solution of acrylic acid (46 g) and 20.1% (w/w) aqueous solution of sodium hydroxide (76.3 g) to neutralize 75 mol% of the acrylic acid, and a temperature in the system was adjusted to 10°C upon the absorption of the monomer solution to the polymerization solution of the first stage to obtain a water-absorbent resin (143.9 g) containing no fine powder and having a sharp distribution of particle size.

Example 8

According to the same manner as described in Example 2, the polymerization was carried out except that a modified polyethylene wherein anhydrous maleic acid was added (manufactured and sold by Mitsui Petrochemical Industries Co., Ltd. under the trade name of Hi-wax 1105A) (2.76 g) was used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g) to obtain a water-absorbent resin (193.4 g) containing no fine powder and having a sharp distribution of particle size.

Example 9

According to the same manner as described in Example 1, the polymerization was carried out except that sucrose di-tristearate having HLB of 3.0 (manufactured and sold by Mitsubishi Chemical Food Industries Co., Ltd. under the trade name of Sugar Ester S-370) (1.38 g) was used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g) to obtain a water-absorbent resin (190.7 g) having no fine powder and a sharp distribution of particle size.

Example 10

According to the same manner as described in Example 1, the polymerization was carried out except that ethyl cellulose (manufactured and sold by Heracules Co., Ltd. under the trade name of Ethyl Cellulose N-22) (2.76 g) was

used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g), cyclohexane was used in place of n-heptane as the solvent, and a temperature in the system was adjusted to 10°C upon the absorption of a partially neutralized acrylic acid solution used in the polymerization of the second stage to the polymerization solution of the first stage to obtain a water-absorbent resin (193.2 g) having no fine powder and a sharp distribution of particle size.

Example 11

According to the same manner as described in Example 9, the polymerization was carried out except that a partially neutralized acrylic acid solution used for the polymerization of the second stage was prepared by mixing a 80% (w/w) aqueous solution of acrylic acid (184 g) and a 20.1% (w/w) aqueous solution of sodium hydroxide (305.2 g) to neutralize 75 mol% of the acrylic acid and then potassium persulfate was added thereto to obtain a water-absorbent resin (287.0 g) having no fine powder and a sharp distribution of particle size.

Example 12

According to the same manner as described in Example 9, the polymerization was carried out except that polyethylene (n=14) glycol diacrylate (each 27.6 mg) was added as a crosslinking agent to both partially neutralized acrylic acid solutions used for both polymerizations of the first and the second stage to obtain a water-absorbent resin (191.3 g) having no fine powder and a sharp distribution of particle size.

Example 13

According to the same manner as described in Example 9, the polymerization was carried out except that N,N'-methylene bisacrylamide (each 18.4 mg) was added as a crosslinking agent both partially neutralized acrylic acid solutions used for the polymerization of the first and the second stages to obtain a water-absorbent resin (192.6 g) having no fine powder and a sharp distribution of particle size.

Example 14

According to the same manner as described in Example 2, the polymerization was carried out except that 28% (w/w) aqueous solution of methacrylamide (310.7 g) was used in place of the partially neutralized acrylic acid solution used for the polymerization of the second stage to obtain a water-absorbent resin (188.5 g) having no fine powder and a sharp distribution of particle size.

Example 15

According to the same manner as described in Example 13, the polymerization was carried out except that 25% (w/w) aqueous solution of N,N-dimethylacrylamide (404.8 g) was used in place of the partially neutralized acrylic acid solution used for the polymerization of the second stage to obtain a water-absorbent resin (203.3 g) having no fine powder and a sharp distribution of particle size.

Example 16

According to the same manner as described in Example 2, the polymerization was carried out except that 30% (w/w) aqueous solution of acrylamide (242 g) was used in place of the partially neutralized acrylic acid solution used for the polymerization of the first stage and N,N'-methylene bisacrylamide (each 18.4 mg) was used in place of ethylene glycol diglycidyl ether used for both polymerizations of the first and second stages to obtain a water-absorbent resin (172.9 g) having no fine powder and a sharp distribution of particle size.

Example 17

According to the same manner as described in Example 2, the polymerization was carried out except that hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (0.92 g) was used in combination with a modified polyethylene wherein anhydrous maleic acid was added (manufactured and sold by Mitsui Petrochemical Industries Co., Ltd. under the trade name of Hi-wax 1105A) (0.92 g) and a temperature in the system was adjusted to 30°C upon absorption of the partially neutralized acrylic acid solution used for the polymerization of the second stage to the polymerization solution of the first stage to obtain a water-absorbent resin (192.4 g) having no fine powder and a sharp distribution of particle size.

Example 18

After completion of the polymerization of the second stage according to Example 1, the resulting polymerization slurry solution was cooled to 20°C. Separately, 80% (w/w) aqueous solution of acrylic acid (92 g) and 20.1% (w/w) aqueous solution of sodium hydroxide (152.6 g) were mixed to neutralize 75 mol% of the acrylic acid. To the mixture was added ethylene glycol diglycidyl ether (36.8 g) and further added potassium persulfate (0.11 g). The resulting partially neutralized acrylic acid solution was added dropwise to the above reaction system and absorbed for 30 minutes. At the same time, the reaction system was thoroughly purged with nitrogen gas. The system was heated and subjected to the polymerization of third stage, while maintaining the bath temperature at 70°C.

Water and n-heptane were distilled off and the residue was dried to obtain a water-absorbent resin (287.5 g) having no fine powder and a sharp distribution of particle size.

Comparative Example 1

N-heptane (550 ml) was placed in a 1 liter four necked cylindrical round bottom flask equipped with a stirrer, a reflux condenser, a dropping funnel and a nitrogen gas inlet. To the flask was added hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g). After heating at 50°C to dissolve the surfactant, the mixture was cooled to 30°C. Separately, 80% (w/w) aqueous solution of acrylic acid (92 g) was placed in a 500 ml conical flask and 20.1% (w/w) aqueous solution of sodium hydroxide (152.6 g) was added dropwise with external ice-cooling to neutralize 75 mol% of the acrylic acid. Potassium persulfate (0.11 g) was added to the mixture and dissolved. The resulting partially neutralized acrylic acid solution was added to the above four necked round bottom flask and the reaction system was thoroughly purged with nitrogen gas. The reaction system was heated and subjected to the polymerization reaction, while maintaining the bath temperature at 70°C. Water and n-heptane were distilled off and the residue was dried to obtain a water-absorbent resin (96.7 g).

Comparative Example 2

According to the same manner as described in Comparative Example 1, the polymerization was carried out except that sorbitan monostearate having HLB of 4.7 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion SP-60R) (2.76 g) was used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g) to obtain a water-absorbent resin (98.2 g).

Comparative Example 3

According to the same manner as described in Comparative Example 1, the polymerization was carried out except that sorbitan monolaurate having HLB of 8.6 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion LP-20R) (0.97 g) was used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g) to obtain a water-absorbent resin (96.0 g).

Comparative Example 4

According to the same manner as described in Comparative Example 1, the polymerization was carried out except that modified polyethylene wherein anhydrous maleic acid was added (manufactured and sold by Mitsui Petrochemical Industries Co., Ltd. under the trade name of Hi-wax 1105A) (2.76 g) was used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g) to obtain a water-absorbent resin (98.0 g).

Comparative Example 5

According to the same manner as described in Comparative Example 1, the polymerization was carried out except that sucrose di-tristearate having HLB of 3.0 (manufactured and sold by Mitsubishi Chemical Food Industries Co., Ltd. under the trade name of Sugar Ester S-370) (1.38 g) was used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g) to obtain a water-absorbent resin (97.1 g).

Comparative Example 6

According to the same manner as described in Comparative Example 1, the polymerization was carried out except that ethyl cellulose (manufactured and sold by Heracules Co., Ltd. under the trade name of Ethyl Cellulose N-22) (2.76 g) was used in place of hexaglyceryl monobehenylate having HLB of 13.1 (manufactured and sold by Nippon Oil and Fats Co., Ltd. under the trade name of Nonion GV-106) (1.38 g) and cyclohexane was used in place of n-heptane to obtain a water-absorbent resin (98.2 g).

Comparative Example 7

According to the same manner as described in Example 1, the polymerization was carried out except that the temperature in the system was adjusted to 45°C upon absorption of a partially neutralized acrylic acid solution used for the polymerization of the second stage to the polymerization solution of the first stage to obtain a water-absorbent resin (192.5 g).

Properties of water-absorbent resins obtained in the above Examples and Comparative Examples are shown in Table 1 below.

Table 1

	Absorbency (g/g)	Water-absorption rate (wettability) (sec.)	Integrity (%)	Reversion (g)	Diffusion (cm)	Average particle size (μm)	Fine powder F100 μm (%)
Ex. 1	70	5	92	0.5	30	450	0.1
Ex. 2	55	4	85	0.2	29	420	0.3
Ex. 3	72	5	93	0.7	33	520	0.0
Ex. 4	50	6	78	1.0	28	370	1.1
Ex. 5	48	6	74	1.8	27	390	0.9
Ex. 6	69	9	70	3.3	27	310	12.1
Ex. 7	75	2	90	4.0	26	340	5.1
Ex. 8	58	6	83	0.3	32	600	0.0
Ex. 9	71	5	90	0.7	28	400	0.4
Ex. 10	68	3	94	0.6	29	390	2.1
Ex. 11	67	3	92	0.5	30	490	0.6
Ex. 12	54	4	87	0.6	27	360	1.3
Ex. 13	59	4	89	0.4	28	380	0.8
Ex. 14	49	4	77	1.5	26	320	2.3
Ex. 15	50	4	78	0.8	26	310	2.7
Ex. 16	52	5	83	0.9	27	410	0.8

Table 1 (continued)

	Absorbency (g/g)	Water-absorption rate (wettability) (sec.)	Integrity (%)	Reversion (g)	Diffusion (cm)	Average particle size (μm)	Fine powder F100 μm (%)
Ex. 17	56	4	83	0.3	30	370	1.3
Ex. 18	67	3	90	0.4	30	470	0.2
Comp. Ex. 1	72	25	43	4.5	25	200	12
Comp. Ex. 2	70	30	35	7.4	22	95	69.3
Comp. Ex. 3	75	8	68	15.9	18	250	15
Comp. Ex. 4	81	35	47	5.5	23	260	14
Comp. Ex. 5	73	29	38	5.0	21	190	26
Comp. Ex. 6	74	12	69	4.7	24	270	7
Comp. Ex. 7	70	7	71	5.1	23	195	17

The water-absorbent resin obtained by the process of the present invention is suitable in the fields of sanitation, soil conditioning and in industry, particularly, in sanitation. That is, since the water-absorbent resin obtained by the process

of the present invention has large particle size, less fine powder and a sharp distribution of particle size, it has the following advantages. Firstly, in diapers for example, reversion is inhibited and diffusion of substances absorbed occurs very well. Secondly, when fixing the water-absorbent resin in a pulp, hardly any water-absorbent resin falls off and a good absorbent article can be obtained. Thirdly, when spreading the water-absorbent resin with a spreader, non-uniform spreading is prevented and it is easy to maintain a constant spread. Furthermore, since the amount of surfactant or polymeric protective colloid in the surface layer of the water-absorbent resin is small, the initial water-absorption rate, i.e., wettability is improved. Furthermore, when fixing the water-absorbent resin to a pulp, integrity of the water-absorbent resin with the pulp is improved and an absorbent article from which hardly any resin falls off is obtained. In addition, since productivity is improved, a cheap water-absorbent resin can be provided. As described hereinabove, the water-absorbent resin obtained by the process of the present invention has excellent properties in, particularly, the field of sanitation because of its various advantages.

Claims

1. A process for the production of a water-absorbent resin, which process comprises, in a first polymerization stage, subjecting an aqueous solution of a water-soluble ethylenic unsaturated monomer to a reversed phase suspension polymerization reaction in a petroleum hydrocarbon solvent in the presence of a surfactant and/or polymeric protective colloid, which surfactant and/or polymeric protective colloid is present in an amount of from 0.1 to 5 wt%, based on the total weight of the aqueous monomer solution of the first stage using a radical polymerization initiator optionally in the presence of a crosslinking agent, cooling the resulting first stage polymerization reaction system to precipitate the surfactant and/or polymeric protective colloid, and then, for at least a second polymerization stage, adding, at least once, an aqueous solution of a water-soluble ethylenic unsaturated monomer solution containing a radical polymerization initiator and optionally a crosslinking agent to the first stage polymerization reaction system to carry out a further reversed phase suspension polymerization reaction.

2. A process according to claim 1, which is carried out in only two polymerization stages and wherein the amount of aqueous solution of the water-soluble ethylenic unsaturated monomer solution containing the radical polymerization initiator and optionally the crosslinking agent added to the first stage polymerization reaction system, for the second polymerization stage, is 50 to 300% by weight based on the weight of the monomer solution for the first polymerization stage.

3. A process according to claim 1 or 2 wherein the water-soluble ethylenic unsaturated monomer in each polymerization stage is acrylic acid, methacrylic acid or an alkali salt thereof.

4. A process according to claim 1 or 2, wherein the water-soluble ethylenic unsaturated monomer in each polymerization stage is acrylamide, methacrylamide or N,N-dimethylacrylamide.

5. A process according to any preceding claim, wherein the surfactant is a nonionic surfactant, or a combination of a nonionic surfactant and an anionic surfactant.

6. A process according to claim 5, wherein the non-ionic surfactant is one or more of sorbitan fatty acid esters, polyglycerin fatty acid esters, sucrose fatty acid esters and sorbitol fatty acid esters.

7. A process according to any preceding claim, wherein the polymeric protective colloid is one or more of ethyl cellulose, ethyl hydroxyethyl cellulose, oxidized polyethylene, polyethylene modified with maleic anhydride, polybutadiene modified with maleic anhydride and ethylene-propylene-diene-terpolymer modified with maleic anhydride.

8. A process according to any preceding claim, wherein the petroleum hydrocarbon solvent is one or more of n-hexane, n-heptane, cyclohexane, toluene and xylene.

9. A process according to claim 8, wherein the petroleum hydrocarbon solvent is n-heptane.

10. A process according to any preceding claim, wherein the aqueous solution of water-soluble ethylenic unsaturated monomer used in each stage contains the monomer in a concentration of not less than 25% by weight.

11. A process according to any preceding claim, wherein the radical polymerization initiator is potassium persulfate.

12. A process according to any preceding claim, wherein the crosslinking agent is ethylene glycol diglycidyl ether or polyethylene glycol diglycidyl ether.

13. A process according to any one of claims 1 to 11, wherein the crosslinking agent is ethylene glycol diacrylate, ethylene glycol dimethacrylate, polyethylene glycol diacrylate or polyethylene glycol dimethacrylate.

14. A process according to any one of claims 1 to 11, wherein the crosslinking agent is N,N'-methylene bisacrylamide.

15. A process according to any preceding claim, wherein the reversed phase suspension polymerization reaction is carried out in three or more stages.

Patentansprüche

1. Verfahren zur Herstellung eines wasserabsorbierenden Harzes, umfassend: eine erste Polymerisationsstufe, in der eine wässrige Lösung eines wasserlöslichen, ethylenisch ungesättigten Monomers einer Umkehrphasen (reversed phase)-Suspensionspolymerisationsreaktion in einem Ölkohlenwasserstoff-Lösungsmittel in Gegenwart eines Benetzungsmittels und/oder eines polymeren Schutzkolloids unterzogen wird, wobei das Benetzungsmittel und/oder das polymere Schutzkolloid in einer Menge von 0,1 bis 5 Gew.% auf Basis des Gesamtgewichts der wässrigen Monomerlösung der ersten Stufe vorhanden ist, unter Verwendung eines Radikalpolymerisationsinitiators, wahlweise in Gegenwart eines Vernetzungsmittels, Kühlung des resultierenden Erststufen-Polymerisationsreaktionssystems, wodurch das Benetzungsmittel und/oder das polymere Schutzkolloid ausgefällt wird, und anschliessend mindestens eine zweite Polymerisationsstufe, mit mindestens einmaliger Zugabe einer wässrigen Lösung eines wasserlöslichen, ethylenisch ungesättigten Monomers, die einen Radikalpolymerisationsinitiator und wahlweise ein Vernetzungsmittel enthält, zu dem Erststufen-Polymerisationsreaktionssystem, wodurch eine weitere Umkehrphasen-Suspensionspolymerisationsreaktion durchgehührt wird.

2. Verfahren gemäss Anspruch 1, dadurch **gekennzeichnet,** dass es in nur zwei Polymerisationsstufen durchgeführt wird, und dass die Menge der wässrigen Lösung der Lösung des wasserlöslichen, ethylenisch ungesättigten Monomers, die den Radikalpolymerisationsinitiator und wahlweise das Vernetzungsmittel enthält, die dem Erststufen-Polymerisationsreaktionssystem in der zweiten Polymerisationsstufe hinzugegeben wird, 50 bis 300 Gew.% auf Basis der Monomerlösung der ersten Polymerisationsstufe beträgt.

3. Verfahren gemäss Anspruch 1 oder 2, dadurch **gekennzeichnet,** dass das wasserlösliche, ethylenisch ungesättigte Monomer in jeder Polymerisationsstufe Acrylsäure, Methacrylsäure oder ein Alkalisalz davon ist.

4. Verfahren gemäss Anspruch 1 oder 2, dadurch **gekennzeichnet,** dass das wasserlösliche, ethylenisch ungesättigte Monomer in jeder Polymerisationsstufe Acrylamid, Methacrylamid oder N,N-Dimethylacrylamid ist.

5. Verfahren gemäss mindestens einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet,** dass das Benetzungsmittel ein nicht-ionisches Benetzungsmittel oder eine Kombination aus einem nicht-ionischen Benetzungsmittel und einem anionischen Benetzungsmittel ist.

6. Verfahren gemäss Anspruch 5, dadurch **gekennzeichnet,** dass das nicht-ionische Benetzungsmittel eines oder mehrere ist, ausgewählt aus Sorbitan-Fettsäureestern, Polyglycerin-Fettsäureestern, Sucrose-Fettsäureestern und Sorbitol-Fettsäureestern.

7. Verfahren gemäss mindestens einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet,** dass das polymere Schutzkolloid eines oder mehrere ist, ausgewählt aus Ethylcellulose, Ethylhydroxyethylcellulose, oxidiertem Polyethylen, mit Maleinsäureanhydrid modifiziertem Polyethylen, mit Maleinsäureanhydrid modifiziertem Polybutadien und mit Maleinsäureanhydrid modifiziertem Ethylen-Propylen-Dien-Terpolymer.

8. Verfahren gemäss mindestens einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet,** dass das Ölkohlenwasserstoff-Lösungsmittel eines oder mehrere ist, ausgewählt aus n-Hexan, n-Heptan, Cyclohexan, Toluol und Xylol.

9. Verfahren gemäss Anspruch 8, dadurch **gekennzeichnet,** dass das Ölkohlenwasserstoff-Lösungsmittel n-Heptan ist.

10. Verfahren gemäss mindestens einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet,** dass die wässrige Lösung des in jeder Stufe verwendeten wasserlöslichen, ethylenisch ungesättigten Monomers, das Monomer in einer Konzentration von nicht weniger als 25 Gew.% enthält.

11. Verfahren gemäss mindestens einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet,** dass der Radikalpolymerisationsinitiator Kaliumpersulfat ist.

12. Verfahren gemäss mindestens einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet,** dass das Vernetzungsmittel Ethylenglykoldiglycidylether oder Polyethylenglykoldiglycidylether ist.

13. Verfahren gemäss mindestens einem der Ansprüche 1 bis 11, dadurch **gekennzeichnet,** dass das Vernetzungsmittel Ethylenglykoldiacrylat, Ethylenglykoldimethacrylat, Polyethylenglykoldiacrylat oder Polyethylenglykoldimethacrylat ist.

14. Verfahren gemäss mindestens einem der Ansprüche 1 bis 11, dadurch **gekennzeichnet,** dass das Vernetzungsmittel N,N'-Methylenbisacrylamid ist.

15. Verfahren gemäss mindestens einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet,** dass die Umkehrphasen-Suspensionspolymerisationsreaktion in drei oder mehr Stufen durchgeführt wird.

Revendications

1. Procédé pour la production d'une résine pour l'absorption de l'eau, comprenant une première étape de polymérisation consistant à soumettre une solution aqueuse d'un monomère insaturé éthylénique hydrosoluble à une réaction de polymérisation en suspension en phase inverse dans un solvant de type hydrocarbure en présence d'un tensio-actif et/ou d'un colloïde protecteur polymère, lequel tensio-actif et/ou colloïde protecteur polymère est présent à raison de 0,1 à 5 % en poids par rapport au poids total de la solution aqueuse du monomère de la première étape, en utilisant un initiateur de polymérisation radicalaire éventuellement en présence d'un agent réticulant, à refroidir le milieu réactionnel résultant de la première étape de polymérisation de façon à faire précipiter le tensio-actif et/ou colloïde protecteur polymère, et ensuite, au moins une seconde étape de polymérisation consistant à ajouter, au moins une fois, une solution aqueuse d'un monomère insaturé éthylénique hydrosoluble contenant un initiateur de polymérisation radicalaire et éventuellement un agent réticulant au milieu réactionnel de la première étape de polymérisation de façon à poursuivre la réaction de polymérisation en suspension en phase inverse.

2. Procédé selon la revendication 1 mettant en oeuvre exclusivement deux étapes de polymérisation, dans lequel la quantité de solution aqueuse du monomère insaturé éthylénique hydrosoluble contenant l'initiateur de polymérisation radicalaire et éventuellement l'agent réticulant, ajoutée au milieu réactionnel de la première étape de polymérisation, lors de la deuxième étape de polymérisation, est comprise entre 50 et 300 % en poids par rapport au poids total de la solution du monomère de la première étape de polymérisation.

3. Procédé selon la revendication 1 ou 2, dans lequel le monomère insaturé éthylénique hydrosoluble est, à chaque étape de polymérisation, l'acide acrylique, l'acide méthacrylique ou un sel de métal alcalin de ceux-ci.

4. Procédé selon la revendication 1 ou 2, dans lequel le monomère insaturé éthylénique hydrosoluble est, à chaque étape de polymérisation, l'acrylamide, le méthacrylamide, ou le N,N-diméthylacrylamide.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le tensio-actif est un tensio-actif non ionique ou une combinaison d'un tensio-actif non ionique et d'un tensio-actif anionique.

6. Procédé selon la revendication 5, dans lequel le tensio-actif non ionique est un ou plusieurs des composés suivants : esters d'acide gras et de sorbitanne, esters d'acide gras et de polyglycérol, esters d'acide gras et de saccharose et esters d'acide gras et de sorbitol.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le colloïde protecteur polymère est un ou plusieurs des composés suivants : éthylcellulose, éthyl-hydroxyéthyl-cellulose, polyéthylène oxydé, polyéthylène modifié par l'anhydride maléique, polybutadiène modifié par l'anhydride maléique et terpolymère éthylène-propylène-diène modifié par l'anhydride maléique.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le solvant de type hydrocarbure est un ou plusieurs solvants choisi(s) parmi le n-hexane, le n-heptane, le cyclohexane, le toluène et le xylène.

9. Procédé selon la revendication 8, dans lequel le solvant de type hydrocarbure est le n-heptane.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel la solution aqueuse du monomère insaturé éthylénique hydrosoluble utilisée à chaque étape contient le monomère en une concentration qui n'est pas inférieure à 25 % en poids.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'initiateur de polymérisation radicalaire est le persulfate de potassium.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'agent réticulant est l'éther diglycidylique de l'éthylèneglycol ou l'éther diglycidylique du polyéthylèneglycol.

13. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel l'agent réticulant est le diacrylate d'éthylèneglycol, le diméthacrylate d'éthylèneglycol, le diacrylate de polyéthylèneglycol ou le diméthacrylate de polyéthylèneglycol.

14. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel l'agent réticulant est le N,N'-méthylène bisacrylamide.

15. Procédé selon l'une quelconque des revendications précédentes, dans lequel la réaction de polymérisation en suspension en phase inverse est réalisée en trois ou plusieurs étapes.